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Degradation of [^{14}C]Terbuthylazine and [^{14}C]Atrazine in Laboratory Soil Microcosms

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Abstract: The degradation and formation of major chlorinated metabolites of terbuthylazine and atrazine in three soils (loamy clay, calcareous clay and high clay) were studied in laboratory experiments using molecules labelled with ^{14}C on the *s*-triazine ring. Soil microcosms were treated with the equivalent of 1 kg ha^{-1} of herbicide and incubated in the dark for 45 days at 20($\pm$1)°C. The quantity of [^{14}C]carbon dioxide evolved in the soils treated with atrazine was negligible and could not be attributed to mineralization of the parent molecule. The mineralization of terbuthylazine accounted for 0·9–1·2% of the initial radioactivity. In the soils studied, the extrapolated half-lives varied from 88 to 116 days for terbuthylazine and 66 to 105 days for atrazine, with no significant differences for the three soils and the two molecules. The deethyl metabolites of the two *s*-triazines and the deisopropyl-atrazine metabolite appeared during the incubation in the three soils. The completely dealkylated metabolite was not detected in any of the soils. After 45 days of incubation, the non-extractable soil residues for the high clay, loamy clay and calcareous clay soils represented for terbuthylazine, 33·5, 38·3 and 43·1% and for atrazine, 19·8, 20·8 and 22·3% of the initial radioactivity.

Key words: atrazine, terbuthylazine, degradation, soils, metabolite formation, non-extractable residues

1 INTRODUCTION

An increasing number of studies reveal contamination of rivers[1] and groundwater[2,3] by atrazine at concentrations higher than the potable limit of 0·1 μg litre^{-1}.[4,5] The use of atrazine has therefore been reduced from 3000 g ha^{-1} to 1500 g ha^{-1} in France, and prohibited in Germany since 1991, where it has been replaced by terbuthylazine. One laboratory study with soil columns under saturated conditions[6] has shown a greater migration of atrazine than of terbuthylazine. Additional studies on comparative movement and degradation are necessary from an environmental point of view in order to assess the positive effects of the replacement of atrazine by terbuthylazine.

The objective of this work was to compare the persistence of the two herbicides in three different soils, providing data essential for the evaluation of their potential dispersion and contamination of groundwater. The various forms of the herbicides were monitored under laboratory conditions: parent molecule, degradation products, carbon dioxide and non-extractable *s*-triazine residues. Each of these different forms (except for carbon dioxide) contributes to environmental contamination.

2 MATERIALS AND METHODS

2.1 Chemicals

Terbuthylazine (N^2-*tert*-butyl-6-chloro-N^4-ethyl-1,3,5-triazine-2,4-diamine) and atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine) molecules were uniformly labelled with ^{14}C on the *s*-triazine ring with specific radioactivities of 995 MBq mmol^{-1} and

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659 MBq $mmol^{-1}$, respectively. The radiochemical purity was >98% for terbuthylazine and >98·6% for atrazine. The water solubility of terbuthylazine is 8·5 mg $litre^{-1}$, while that of atrazine is 28 mg $litre^{-1}$.

2.2 Soils

Three agricultural soils from the *Region Centre* near Orléans in France were used for this study. Samples were taken in the surface horizon (0–30 cm), air dried, homogenized and sieved at 3·15 mm. The main characteristics of these soils are given in Table 1.

2.3 Incubation set-up

The aggregates of soil smaller than 1 mm were eliminated by sieving in order to avoid anaerobic conditions unfavourable to microbial activity and rarely present in ploughed agricultural soil. This does not modify the physicochemical characteristics (granulometry, organic carbon content and calcium carbonate content) of the soils because the 1–3·15-mm soil fraction has the same physicochemical characteristics as the fraction of aggregates smaller than 3·15 mm (unpublished data).

After manual homogenization of the sample, 35-g portions of dry soil were put into crystallizers, 46 mm diameter. The field water capacities, measured using a pressure membrane at pF 3 (100 kPa) were 23%, 26% and 35% for the loamy clay, calcareous clay and high clay soils, respectively. The soil moisture was set at 80% of the field capacity by a solution of herbicide in water + methanol (90 + 10 by volume) of a concentration adequate to add 0·17 mg of herbicide to each sample (i.e. 0·17 mg on 16·61 cm^2, the equivalent of 1 kg ha^{-1} of active ingredient).

Each glass vessel was placed in a glass container (1·5 litre). These airtight containers contained, in addition to the soil sample, a scintillation flask containing sodium hydroxide (0·5 M; 10 ml) in order to trap the [^{14}C]carbon dioxide evolved, and a bottle of water to minimize variations in water content. The air was changed when the recipient was opened periodically to measure [^{14}C]carbon dioxide.

The incubator was put in a dark room at a constant temperature of 20 (±1)°C for 45 days. For terbuthylazine, 21 samples of each soil were set in a way that enabled seven soil samples with three replicates to be taken during each incubation period of 3, 6, 12, 19, 25, 35 and 45 days. There were also three blanks without soil. Three samples of each soil to be used for three samplings (not repeated) after 6, 25 and 45 days were treated with 1 kg ha^{-1} of atrazine. This dose, identical to that of terbuthylazine, enabled a direct comparison of the two herbicides to be made. A previous study had also been carried out under these conditions with the same soils, with 2 kg ha^{-1} of atrazine.[7] Results from this previous study were taken into account (i) when we studied the statistical significance of the possible differences between the soils treated with atrazine, because this experiment was done with triplicates of each microcosm for each sampling time, and (ii) in our attempt to determine better the appearance of metabolites with time, because a larger number of samples were taken, notably after the third day of incubation.

2.4 [^{14}C]carbon dioxide measurement

In order to monitor the kinetics of the formation of [^{14}C]carbon dioxide resulting from the degradation of the *s*-triazine ring, duplicate 1-ml samples of sodium hydroxide solution were taken from each microcosm for each of the seven terbuthylazine and three atrazine sampling times, except that the last measurement in each case was made on day 43, not day 45. The radioactivity corresponding to [^{14}C]carbon dioxide was measured by liquid scintillation counting (LSC) of the sodium hydroxide (1 ml) in 'Ultima Gold'™ (10 ml) (Packard) with a Packard Tri-carb 460 CD.

2.5 Extractable [^{14}C]radioactivity analysis

The *s*-triazine residues produced by the degradation of the two active ingredients were extracted from soil

TABLE 1
Soil Characteristics

Soil (*USA taxonomy*)	*pH* (H_2O)	*Sand*[a] (%)	*Silt*[a] (%)	*Clay*[a] (%)	*O.C.*[b] (%)	$CaCO_3$ (%)
Loamy clay (Typic eutrochrept)	8·2	3·6	64·7	31·7	1·11	1·9
Calcareous clay (Mollic eutrochrept)	8·0	29·2	19·5	51·3	1·50	26·4
High clay (Vertic eutrochrept)	8·0	24·5	13·0	62·5	1·08	3·2

[a] Fractionation with Na-saturated amberlite IRN 77 resins.
[b] O.C.: organic carbon content measured through combustion at 940°C using a Carmhograph 12 Wösthoff.

samples (35 g) at room temperature with methanol (3 × 70 ml) by 12-hour rotary agitation. The radioactivity of each extract, and the total radioactivity of the combined extract after mixing of the three extractions was measured by LSC in methanol (1 ml) in 'Ultima Gold'™ (10 ml) using a Packard Tri-carb 460 CD. Soil was sampled for extractions on days 0, 3, 6, 12, 19, 25, 35 and 45 (end of incubation). The extracts were then evaporated to dryness with a rotovapor and dissolved in methanol (4 ml) for analysis.

Atrazine, terbuthylazine and their chlorinated derivatives were analyzed by gas chromatography using a Varian 3300 with a thermosensitive detector (TSD). Operating conditions were: glass column (1·2 m × 2·2 mm ID) packed with chromosorb G 60–80 mesh (2% NPGS); injector, detector, column temperatures at 230°C, 250°C and 200°C respectively; nitrogen carrier gas at 30 ml min^{-1} and air and hydrogen at 180 and 4·5 ml min^{-1}, respectively. The detection limits expressed as a function of soil dry weight (mg kg^{-1}) for identical conditions were 0·015 mg kg^{-1} for atrazine, 0·03 mg kg^{-1} for deethyl-atrazine, 0·04 mg kg^{-1} for deisopropyl-atrazine, 0·10 mg kg^{-1} for diamino-atrazine, 0·01 mg kg^{-1} for terbuthylazine, 0·02 mg kg^{-1} for deethyl-terbuthylazine.

2.6 Non-extractable [^{14}C] residue analysis

After extraction, the soil samples were dried for three to four days in an oven at 30°C and then ground to 50 μm. A well-mixed subsample (1 g) was ashed at 950°C with oxygen flow using a Carmhograph 12 Wösthoff. The carbon dioxide, including [^{14}C]carbon dioxide from the *s*-triazines, was trapped in 2-ethoxyethanol + ethanolamine (8 + 2 by volume; 15 ml). Trapping efficiency of the cocktail was 94·5%. An aliquot of this mixture (10 ml) was added to the 299™ scintillator (10 ml) (Packard) for LSC with a Packard Tri-carb 460 CD. The minimum detectable radioactivity was 1·0 Bq g^{-1} of soil.

3 RESULTS AND DISCUSSION

3.1 Mineralization

For terbuthylazine, a large quantity of [^{14}C]carbon dioxide 0·7–0·9%, was measured from the third day on, after which the quantities evolved decreased until the 15th day (0·16–0·25%) before stabilizing until the end of the incubation (Fig. 1). The first phase, with a strong production of [^{14}C]carbon dioxide, could correspond to a rapid degradation of an impurity resulting from terbuthylazine synthesis. Because the purity of radiolabelled terbuthylazine was greater than 98%, it would

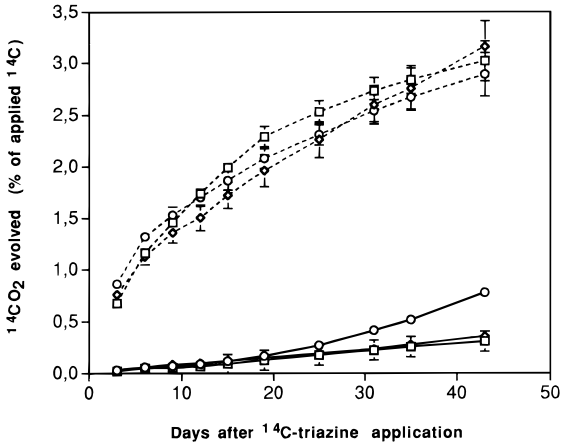

Fig. 1. Cumulative evolution of [^{14}C]carbon dioxide from (○) loamy clay soil, (□) calcareous clay soil and (◇) high clay soil, treated with 1 kg ha^{-1} of (——) [^{14}C]atrazine or (---) [^{14}C]terbuthylazine during a 43-day incubation period. Values are means of triplicate samples with a ± 95% confidence interval.

appear that the 2·9–3·2% [^{14}C]carbon dioxide evolved during the 43 days of incubation corresponds to the mineralization of at least 0·9–1·2% of the terbuthylazine initially added. The lower rate of terbuthylazine mineralization observed by Schroll *et al.*,[8] 0·004% degraded into [^{14}C]carbon dioxide in a seven-day period (0·02% if we extrapolate for 45 days), can be explained by a different microflora developing in a sandy soil with 85% sand (versus loamy clay, calcareous clay and high clay soils in the present study) and by the application of formulated terbuthylazine ('Gardoprim') which might have modified the properties of the active ingredient used as such in our study.

For atrazine, the [^{14}C]carbon dioxide curves increased with time and reached a maximum of 0·3–0·8% of the applied quantity. Soil microcosms treated with [^{14}C]atrazine evolved less than 1% of the total activity as [^{14}C]carbon dioxide during the 43-day incubation period. Since the radiolabelled compounds supplied for the incubation were no purer than 98·6%, [^{14}C]carbon dioxide evolution might be due to mineralization of impurities as well as mineralization of the radiolabelled parent. It was therefore not possible to attribute the observed mineralization entirely to the applied radiolabelled atrazine. On the other hand, Winkelmann and Klaine[6] reported that 2·5–7% of atrazine could be mineralized in 45 days of incubation. The incubation temperature used by these authors, 25°C instead of 20°C, could explain their higher mineralization rate, which might correspond to greater microbial activity. The lower microbial activity in our soils could also be due to the conditioning of the soil, which was dried and stored and rehumidified before incubation. Winkelmann and Klaine[9] preserved the original structure and humidity of their soil samples until incubation, disrupting microbial activity to a lesser extent.

TABLE 2
Evolution of Concentrations of Terbuthylazine, Atrazine and Their Metabolites Measured in Three Soils during a 45-day Incubation Period after Application of 1 kg ha^{-1} of Active Ingredient[a]

	Residue (mg kg^{-1}) after Time (days)						
Soil	*3*	*6*	*12*	*19*	*25*	*35*	*45*
Terbuthylazine							
Loamy clay	5·03a	4·63ab	4·54b	4·82ab	3·99c	3·58d	3·69d
Calcareous clay	4·89a	4·62ab	4·53b	4·40ab	4·13c	3·94d	3·80d
High clay	4·77a	4·66ab	4·64b	4·77ab	4·35c	3·71d	3·64d
Deethyl-terbuthylazine							
Loamy clay	nd[b]	nd	0·02a	0·07c	0·09e	0·11g	0·18i
Calcareous clay	nd	nd	0·03a	0·07c	0·09e	0·14g	0·17i
High clay	nd	nd	0·04b	0·09d	0·11f	0·15h	0·09j
Atrazine							
Loamy clay		4·69			4·08		3·73
Calcareous clay		5·11			4·24		3·67
High clay		5·09			4·31		3·75
Deethyl-atrazine							
Loamy clay		0·07			0·08		0·28
Calcareous clay		0·04			0·09		0·21
High clay		nd			0·14		0·41
Deisopropyl-atrazine							
Loamy clay		nd			0·04		0·07
Calcareous clay		nd			0·04		0·10
High clay		nd			0·06		0·10

[a] Values followed by the same letter for a given compound do not differ at the 5% level using Newman-Keuls test of a factorial ANOVA (time and soil). Soil microcosms treated with atrazine were not replicated.
[b] Nd: not detectable.

TABLE 3
First-Order Kinetics Parameters for loss of Terbuthylazine and Atrazine from the Three Soils

Soil	C_O [a] (*% of initial amount*)	k ($\times 10^3$)[a] (day^{-1})	$t_{1/2}$ (*days*)	r^2
Terbuthylazine				
Loamy clay	0·87	7·85	88	0·998
	(0·82–0·92)	(5·03–10·67)	(65–138)	
Calcareous clay	0·85	5·95	116	0·999
	(0·84–0·87)	(5·15–6·76)	(102–134)	
High clay	0·85	6·74	103	0·998
	(0·81–0·89)	(4·52–8·96)	(77–153)	
Atrazine				
Loamy clay	0·98	6·60	105	0·999
	(0·95–1·02)	(5·16–8·03)	(86–134)	
Calcareous clay	0·97	10·36	66	0·999
	(0·98–1·05)	(8·19–12·54)	(55–85)	
High clay	1·02	6·68	104	0·999
	(0·99–1·05)	(5·32–8·03)	(86–130)	

[a] Values in parentheses are 95% confidence intervals.

TABLE 4
^{14}C Mass Balance in Soil Microcosms Treated with Labelled Terbuthylazine[a]

	(*Percentage of total ^{14}C in various fractions*)				
Time (days)	*Extractable radioactivity*	*$^{14}CO_2$ evolved*	*Non-extractable residues[b]* A	B	*Total*
Loamy clay soil					
0	87·0	—[c]	—	—	—
3	87·27 (± 1·09)	0·86 (± 0·05)	20·98 (± 2·00)	7·98	109·11
6	81·40 (± 6·65)	1·32 (± 0·05)	24·72 (± 1·82)	11·72	107·44
12	79·33 (± 11·30)	1·70 (± 0·05)	26·91[d]	13·91	107·94
19	74·00 (± 2·55)	2·08 (± 0·06)	30·83 (± 3·10)	17·83	106·91
25	73·96 (± 1·61)	2·31 (± 0·06)	33·53 (± 1·64)	20·53	109·80
35	70·62 (± 2·19)	2·67 (± 0·05)	35·14 (± 2·73)	22·14	108·43
45	65·38 (± 9·26)	2·89 (± 0·02)	38·28 (± 4·92)	25·28	106·55
Calcareous clay soil					
0	86·0	—	—	—	—
3	85·52 (± 5·04)	0·68 (± 0·03)	23·04 (± 3·61)	9·06	109·24
6	82·50 (± 1·00)	1·16 (± 0·04)	27·37 (± 0·58)	13·37	111·03
12	78·04 (± 2·03)	1·74 (± 0·03)	30·73 (± 1·91)	16·73	110·51
19	74·40 (± 1·61)	2·29 (± 0·05)	33·88 (± 2·82)	19·88	110·57
25	72·04 (± 2·82)	2·53 (± 0·04)	36·64 (± 1·09)	22·64	111·21
35	68·55 (± 2·58)	2·84 (± 0·06)	39·78 (± 3·43)	25·78	111·17
45	65·04 (± 4·04)	3·02 (± 0·05)	43·11 (± 2·95)	29·11	111·17
High clay soil					
0	85·0	—	—	—	—
3	81·42 (± 3·16)	0·76 (± 0·05)	20·52 (± 8·93)	5·52	102·70
6	80·67 (± 0·52)	1·13 (± 0·07)	20·73 (± 4·10)	5·73	102·53
12	72·25 (± 8·66)	1·51 (± 0·12)	23·62[d]	8·62	97·38
19	72·70 (± 0·46)	1·99 (± 0·21)	26·34 (± 6·80)	11·34	101·03
25	71·87 (± 1·24)	2·29 (± 0·22)	29·12 (± 2·22)	14·12	103·28
35	63·66 (± 2·89)	2·79 (± 0·20)	31·81 (± 2·70)	16·81	98·26
45	65·32 (± 0·27)	3·21 (± 0·39)	33·54 (± 1·21)	18·54	102·07

[a] Values are means of triplicate samples (±95% confidence interval).
[b] A Raw data. B Corrected for percentage recovery at $t = 0$.
[c] Not measured.
[d] Confidence intervals are not given for these values because there were only two measurements.

3.2 Persistence and parent molecule dissipation

The terbuthylazine concentration in the soil decreased from 5·0 mg kg^{-1} on day 3 to 3·7 mg kg^{-1} at the end of the incubation period (Table 2), without any significant difference between the three soils. A similar decrease was observed for atrazine.[7]

The persistance of the two *s*-triazines can be compared by using first-order kinetics in which the degradation rate is directly proportional to the percentage of recovery:

$$C = C_0 e^{-kt}$$

where C is the percentage recovery of parent molecule at time t (days), C_0 is the percentage recovery at time 0, k is the rate constant (day^{-1}).

The extrapolated half-lives vary between 88 and 116 days for terbuthylazine and between 66 and 105 days for atrazine, without any significant difference between the three soils and the two molecules (Table 3). Under similar incubation conditions, Dibbern and Pestemer[10] obtained a similar half-life of 68 days for terbuthylazine in a loamy soil with a 1·3% organic carbon content. For an incubation temperature of 25°C, Obrador *et al.*[11] calculated half-life values of 55 days for atrazine in a loamy soil with 0·5% of organic carbon. This figure, which is lower than ours, could be explained by a higher temperature more favourable to molecular degradation.

3.3 Metabolite formation

The decrease in terbuthylazine concentration was accompanied by an increase in deethyl-terbuthylazine concentration (Table 2). This metabolite was detected from the 12th day of incubation of concentrations of 0·02 mg kg^{-1} for the loamy clay, 0·03 mg kg^{-1} for the calcareous clay and 0·04 mg kg^{-1} for the high clay soil.

TABLE 5
^{14}C Mass Balance in Soil Microcosms Treated with Labelled Atrazine[a]

	(*Percentage of total* ^{14}C)				
	Extractable radioactivity	$^{14}CO_2$ *evolved*	*Non-extractable residues* A	B	*Total*
Loamy clay soil					
0	99·80	—[c]	—	—	—
6	96·56	0·05	6·08	5·88	102·69
25	82·35	0·27	14·76	14·56	97·38
45	79·12	0·78	20·81	20·61	100·71
Calcareous clay soil					
0	101·0	—	—	—	—
6	93·36	0·05	7·50	7·50	100·91
25	84·82	0·17	16·05	16·05	101·04
45	76·46	0·31	22·31	22·31	99·08
High clay soil					
0	99·60	—	—	—	—
6	94·33	0·06	5·72	5·32	100·11
25	86·29	0·19	15·48	15·08	101·96
45	77·52	0·36	19·79	19·39	97·67

[a] The soil microcosms were not replicated.
[b] A Raw data. B Corrected for percentage recovery at $t = 0$.
[c] Not measured.

The deethyl-terbuthylazine concentration increased during the 45-day incubation period to a level of 0·18 mg kg^{-1} for all three soils. There was little significant difference in deethyl-terbuthylazine formation between the three soils (Table 2). The two other chlorinated metabolites of terbuthylazine were not detected in any of the incubated soils.

For soils treated with 1 kg ha^{-1} of atrazine, deethyl- and deisopropyl-atrazine were detected from the 6th and the 25th day on, respectively (Table 2). In the incubation with 2 kg ha^{-1}, traces of deethyl- and deisopropyl-atrazine were also found, albeit sooner.[7] Most likely, this was because of the higher application dose, resulting in degradation products appearing more rapidly in quantities sufficient to be detected. For the 1 kg ha^{-1} treatment, more of the deethyl derivative formed than the deisopropyl derivative (Table 2), in agreement with the results of Winkelmann and Klaine.[9] The diamino derivative was, as was the case for samples treated here with terbuthylazine, absent from samples treated with atrazine. The absence of the completely dealkylated metabolite was also observed by Winkelmann and Klaine.[9] These results indicate that the greater the steric hindrance of the carbon group, the harder it is for microorganisms to break the alkyl chains. Groups are more easily broken in the following order: ethyl > isopropyl > *tert*-butyl. Esser *et al.*[12] observed that the longer the carbon chain, the harder it was to break the alkyl group. In our study, metabolite concentration increased with time (Table 2), while Winkelmann and Klaine[9] reported a decrease in deethyl and deisopropyl derivative concentrations after the 14th day of incubation. This decrease might be due to a reduction in microbial activity in the case of Winkelmann and Klaine's incubation.

Smaller quantities of deethyl metabolite were formed from terbuthylazine than from atrazine. The greater adsorption of terbuthylazine on the three soils, with K_f values ranging from 1·88 to 2·33, compared to values of 0·96 to 1·22 for atrazine,[13] would protect the molecule from microbial attack. This phenomenon has been reported by Hance[14] and Barriuso *et al.*[15] This greater adsorption of terbuthylazine may also explain why deethyl-terbuthylazine appears later than deethyl-atrazine.

Calculation of the mass balance shows that the decrease in recovery of the two *s*-triazines was not compensated for by the formation of their respective metabolites (Table 2), nor by mineralization of the *s*-triazine ring, which accounted for less than 1% of the added radioactivity. This might be explained by a progressive immobilization of the parent molecule and its derivatives.[16]

3.4 Non-extractable residues

While extractability was decreasing to around 65% by the 45th day of incubation for terbuthylazine and 77% for atrazine, the residual radioactivity in the soil measured by combustion increased for the two triazines and reached, after 45 days of incubation, 33·5, 38·3 and 43·1% of the initial radioactivity of the added terbuthy-

lazine, for the high clay soil, loamy clay soil and calcareous clay soil, respectively (Tables 4 and 5). Residual radioactivity values were lower for atrazine: 19·8, 20·8 and 22·3% of the initially added ^{14}C for the same soils.

Values for extractable radioactivity and non-extractable residues were not significantly different for the three soil types for terbuthylazine (Table 4), nor for atrazine (Table 5).

At $t = 0$ in the three soils, 100% of the atrazine radioactivity was extractable, compared to only 86% of that of terbuthylazine. This difference in extraction efficiency is due either to a higher methanol extraction efficiency for atrazine than for terbuthylazine, or to a stronger adsorption of terbuthylazine. During the incubation period, the extractability of radioactivity decreased in a similar manner for the two pesticides. If the final residual radioactivity values are corrected for the efficiency of methanol extraction, different for the two herbicides, the quantities of non-extractable residue formed are similar for atrazine and terbuthylazine (Tables 4 and 5).

For atrazine, Winkelmann and Klaine[9] obtained non-extractable residue values similar to ours, with 26% for an incubation period of 63 days at 25°C for loamy soils containing 0·5% organic content. There are no reports in the literature of laboratory experiments studying the formation of terbuthylazine residues. Nevertheless, lysimeter experiments on a sandy soil with 1% organic content have shown that 56·5% of the terbuthylazine is non-extractable 244 days after its application.[8] Similar values have been reported for atrazine; (48·5% of the residue was non-extractable 10 months after treatment (502 mm of rainfall) for a calcareous clay soil with 1·2% organic content.[17]

4 CONCLUSIONS

For the soils studied here, degradation of the two *s*-triazine herbicides (i) is slow, with extrapolated half-lives of 88–116 days for terbuthylazine and 66–105 days for atrazine, (ii) results in chlorinated derivatives known to be environmentally hazardous[18] and (iii) leads to a very limited mineralization of terbuthylazine, 0·9 to 1·2%, and insignificant mineralization of atrazine. Large quantities of *s*-triazine derivatives (the parent molecules and their derivatives) therefore remain potentially available in the soils and can be transported towards the groundwater. A large proportion of these *s*-triazine derivatives becomes non-extractable; 33·5–43·1% for terbuthylazine and 19·8–22·3% for atrazine. These non-extractable residues, while more difficult to leach, increase the persistence of the herbicide in the top soil horizons and are a latent source of pollution due to various factors which can cause them to be remobilized in the soil solution.[16,19]

The half-lives of the herbicides and the amounts of non-extractable residues being similar for the two molecules in the three soils, one might tend to conclude, if only degradability was taken into account, that potential contamination of water by these molecules is identical for the three soils. This study was, however, carried out in the laboratory and therefore does not take into account the vertical movement of herbicides which plays a determining role in both the persistance of xenobiotics and in their transport toward groundwater. Complementary studies of leaching must be carried out in order to complete this study of degradation and the previous study of adsorption/desorption of these two herbicides[13] in order to assess their polluting character.

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REFERENCES

1. Squillace, P. J. & Thurman, E. M., Herbicide transport in rivers: importance of hydrology and geochemistry in non point source contamination. *Env. Sci. Technol.*, **26** (1992) 538–45.
2. Domagalski, J. L. & Dubrovsky, N. M., Pesticide residues in ground water of the San Joaquin Valley, California. *J. Hydrology*, **130** (1992) 299–338.
3. Koterba, M. T., Banks, W. S. L. & Shedlock, R. J., Pesticides in shallow groundwater in the Delmarva Peninsula. *J. Environ. Qual.*, **22** (1993) 500–18.
4. European Community, Council Directive on the quality of water for human consumption. *Official Journal of the EC*, 80/778 EEC L229 (1980) 11–29.
5. Décret no 89-3 du 3 janvier 1989 relatif aux eaux destinées à la consommation humaine à l'exclusion des eaux minérales naturelles. *Journal officiel de la République française* (1989) 125–31.
6. Gomez de Barreda, D., Gamon, M., Lorenzo, E. & Saez, A. Residual herbicide movement in soil columns. *Sci. Total Environ.*, **132** (1993) 155–65.
7. Dousset, S., Evaluation des potentialités de lessivage de la terbuthylazine et de l'atrazine dans trois sols de la Région Centre. PhD thesis, INPL, ENSAIA, F-54505 Vandœuvre, 1994, 161 pp.
8. Schroll, R., Langenbach, T., Cao, G., Dörfler, U., Schneider, P. & Scheunert, I., Fate of [^{14}C]terbuthylazine in soil–plant systems, *Sci. Total Environ.*, **123/124** (1992) 377–89.
9. Winkelmann, D. A. & Klaine, S. J., Degradation and bound residue formation of atrazine in a western Tennessee soil. *Environ. Toxicol. Chem.*, **10** (1991) 335–45.
10. Dibbern, V. H. & Pestemer, W., Anwendbarkeit von simulationmodellen zum einwaschungsverhalten von pflanzenschutzmitteln im boden. *Nachrichtenbl. Deut. Pflanzenschutzd.*, **44** (1992) 134–43.
11. Obrador, A., Lechon, Y. & Tadeo, J. L., Simulation of atrazine persistence in Spanish soils. *Pestic. Sci.*, **37** (1993) 301–8.

12. Esser, H. O., Dupuis, G., Ebert, E., Marco, G. & Vogel, C., *S*-Triazines, In Degradation of Herbicides, ed. P. C. Kearney & D. D. Kaufman. Marcel Dekker, Inc., New York, 1975, vol. 1, 130 pp.
13. Dousset, S., Mouvet, C. & Schiavon, M., Sorption of terbuthylazine and atrazine in relation to the physicochemical properties of three soils. *Chemosphere*, **28** (1994) 467–76.
14. Hance, R. J., Influence of sorption on the decomposition of pesticides. *Soc. Chem. Industry Monograph*, **37** (1970) 92–104.
15. Barriuso, E., Deleu, R., Copin, A. & Houot, S., Résidus d'atrazine et de pendiméthaline dans les sols: influence du mode de fertilisation. *Comm. Symp. Inter. Phytopharmacie Phytiatrie*, Gand, Belgique, 1988, 1443–53.
16. Demon, M., Schiavon, M., Portal, J. M. & Munier-Lamy, C., Seasonal dynamics of atrazine in three soils under outdoor conditions. *Chemosphere*, **28** (1994) 453–66.
17. Dousset, S., Mouvet, C. & Schiavon, M., Leaching of atrazine and some of its metabolites in undisturbed field lysimeters of three soil types. *Chemosphere*, **30** (1995) 511–24.
18. Hallberg, G. R., Pesticide pollution of groundwater in the humid United States. *Agric. Ecosyst. Environ.*, **26** (1989) 299–367.
19. Khan, S. U. & Ivarson, K. C., Microbial release of unextracted (bound) residues from an organic soil treated with prometryn. *J. Agric. Food Chem.*, **29** (1981) 1301–3.